

Hybrid organic–inorganic materials containing poled zwitterionic push–pull chromophores

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Abstract

Dihydroxy functionalised zwitterionic push-pull chromophores have been introduced in 3-glycidoxypropyltrimethoxysilane, tetraethylorthosilicate and *N*-[(3-trimethoxysilyl)propyl]ethylenediamine derived hybrid materials. Hybrid films have been deposited as thick layers via spin-coating. The amine groups introduced with the organically modified alkoxide bearing amine functionalities have been found to have an effective scavenger effect of the dye photobleaching. The addition, during the synthesis of the precursor sol, of *N*-hydroxyl carbazole has allowed to reach up to 20% of chromophore concentration avoiding the formation of aggregates within the matrix. The NLO properties of the material, after poling, have shown a good temporal stability, with retention of ca. 70% of the initial signal value, after several months, providing a d_{33} value of $\sim 50 \div 70$ pm V⁻¹ at the wavelength of 1.064 μ m.

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1. Introduction

Organic–inorganic hybrid materials incorporating second and third order non-linear optical (NLO) chromophores, have been largely studied to obtain new photonic materials and devices.¹ In particular, systems containing chromophores with high hyperpolarizability, covalently bonded to the host matrix network, represent an interesting alternative to organic polymers. In fact, the very peculiar properties of hybrid materials, such as a relatively large laser damage threshold, low optical propagation losses, high transparency and easy film processing make this class of materials a very competitive one for photonic applications. The typical soft chemistry of sol-gel processing is a helpful tool, especially for the relatively low-temperature conditions of the synthesis (below 100 °C), compatible with most organic dyes that generally suffer from thermal decomposition. Dye doped materials, to observe macroscopic second-order NLO activity, should exhibit a non-cen-

tro-symmetric orientation of the organic chromophores. This alignment can be achieved through a poling procedure accomplished, for instance, by an electric field.

To meet the actual requirements for electro-optic photonic devices, the second order NLO properties of the material should show a very long-term temporal stability, corresponding to the lowest degree of orientational relaxation. Hybrid sol-gel materials offer the advantage of a large network rigidity, given by the inorganic side of the network, which should lead to good temporal stability.²

In this work, we have developed a system consisting of a hybrid organic-inorganic host material and a chromophore, BisOH.PETCN (Fig. 1), specifically functionalized to be covalently bonded to the inorganic silica network via the reaction of the two hydroxy functionalities. The chromophore,^{3–5} has a much larger hyperpolarizability with respect to the commonly used, DANS (4-dimethylamino-4'-nitrostilbene) or Disperse Red 1. This allowed to obtain large second-order non-linearity even at relatively low chromophore concentration. At the same time, a better control of the dye–matrix interactions allowed to get more stable poled films. As observed in our previous work,⁶ the main

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obstacle to reach large d_{33} values for these materials is the control of the aggregation states at large chromophore concentrations. In fact, dimers or higher order aggregates, are easily formed and decrease the overall NLO efficiency of the system. Reducing the aggregation of the chromophores should allow us to obtain, therefore, large NLO activity. In this paper we report a synthesis that allows us to reduce the aggregation with a strong enhancement of the NLO performances.

2. Experimental

1-[N-(3-bromopropyl)pyrid-4-yl]-2-[5-(dicyanomethanido)thien-2-yl]ethylene, (BisOH.PETCN), (Fig. 1) showing high second-order NLO activity and characterized by an aromatic and highly zwitterionic ground state and a quinoid/neutral excited state⁷ (Fig. 1), was prepared in accordance to the protocol previously reported.²

Tetraethylorthosilicate (TEOS) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) (Aldrich) were co-hydrolyzed ($H_2O:TEOS:GPTMS = 2:0.3:0.7$) in methyl alcohol (MeOH) (Prolabo) and refluxed 1 h at 80 °C (sol GT).

BisOH.PETCN and N-hydroxyl carbazole, in solution with acetic acid and the amine functionalized silica precursor, *N*-[(3-trimethoxysilyl)propyl]ethylenediamine, (TMESPE), were added to GT. The films, about 2 μ m thick, were deposited by spin or dip-coating. The samples were dried in air at different temperatures in the range 50–300 °C. The chromophore BisOH.PETCN was added to reach up to 20% molar concentration with respect to (TMESPE + GPTMS + TEOS) in the matrix, the ratio $TMESPE/(GPTMS + TEOS)$ was 25% or 45%.

Absorption spectra of hybrid doped films, deposited on silica slides, were taken in the range 190–800 nm at room temperature using a Perkin Elmer λ -3B spectrophotometer (resolution 0.3 nm). To test temporal stability, absorption measurements were repeated at different times, storing the samples in the dark. The 20% BisOH.PETCN doped films were poled by means of high-voltage corona poling.^{8,9} The corona discharge was generated, under a nitrogen atmosphere, by a gold wire biased with +7000 V across a 1 cm gap normal to the sol-gel film. Second harmonic generation (SHG) measurements were performed during this procedure and afterwards at regular time intervals by using a

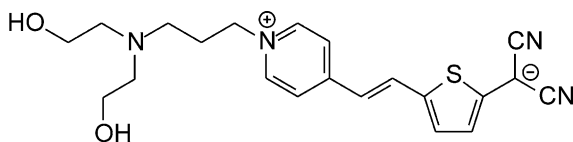


Fig. 1. The zwitterionic push–pull chromophore introduced in the hybrid host materials, 1-[N-(3-N'-diethanolaminopropyl)pyrid-4-yl]-2-[5-(dicyanomethanido)thien-2-yl]ethylene, (BisOH.PETCN).

Q-switched Nd:YAG laser, operating at 1.064 μ m, as the source of the fundamental wave. Angle-resolved absorption measurements were done by polarized light to verify the chromophore alignment.¹³

3. Results and discussion

The compound BisOH.PETCN is part of a class of organic molecules that shows enhanced first molecular hyperpolarizabilities (β as high as $27\,000 \times 10^{-48}$ esu).⁴ A drawback is, however, represented by a poor chemical and thermal stability because BisOH.PETCN is decomposed in the presence of light and oxygen (photobleaching) and is sensitive to acidic environments due to the carbanionic nature of the donor moiety.

The typical UV–Vis absorption spectra of BisOH.-PETCN in hybrid film show two bands (Fig. 2), a broad intense band around 630 nm, assigned to intramolecular charge transfer (ICT) and another band with much lower intensity at 380 nm, attributed to electronic transitions within the aromatic rings. The absorption spectrum of BisOH.PETCN in fresh deposited samples, shows a shoulder around 580 nm (Fig. 2). This band is attributed to chromophore dimers probably formed immediately after the incorporation in the matrix, via bridging molecules of the residual solvent.⁶ These absorption bands, in fact, decrease immediately after the drying process (Fig. 2).⁶

On the other hand, the decrease in intensity of the main band at 630 nm is associated with degradation of the chromophores, which can be originated by thermal degradation or photobleaching effects. However, this decrease in hybrid matrix is rather negligible if compared to the behaviour of pure BisOH.PETCN in a protic solvent where complete photobleaching occurs in a few minutes. In fact, upon incorporation in the hybrid matrix containing the amine functionalities and maintaining the sample in a dark environment, the ICT band results stable for at least 2 months (Fig. 3). The amine

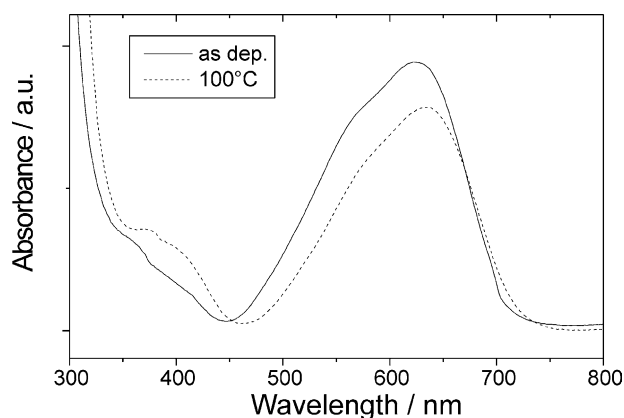


Fig. 2. UV–Vis spectra of hybrid films doped with BisOH.PETCN (5%) as deposited and treated at 100 °C.

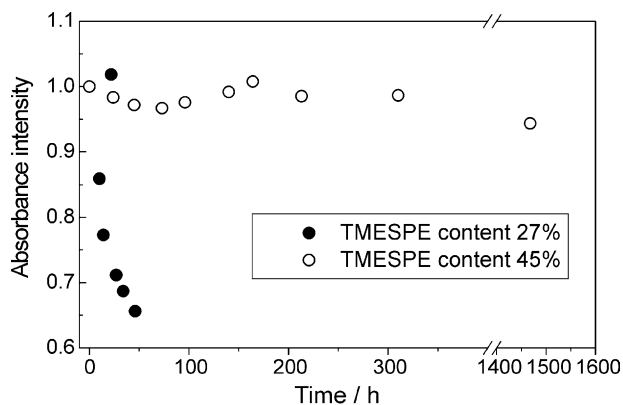


Fig. 3. Time dependence of UV-Vis absorbance (normalized values at $\lambda = 630$ nm) of BisOH.PETCN incorporated in the hybrid matrices (5%) prepared with two amine concentrations.

groups introduced in the matrix via TMESPE as network modifiers, are very effective to inhibit the formation of the singlet oxygen, reducing the photobleaching process. The amines, in fact, facilitate the quenching of the singlet oxygen to the ground triplet state before the attack of the chromophores.¹⁰ At the same time the basic environment created by TMESPE avoids the chemical degradation observed in an acidic media due to the protonation of the carbanionic site of the donor moiety.

Another important result observed is the screening effect of the N-hydroxyl carbazole between the zwitterionic molecules that elsewhere will tend to aggregate. The addition of N-hydroxyl carbazole in the sol significantly reduces the aggregation of BisOH.PETCN, we attribute, in fact, the very much improvement of the d_{33} value of the material, with respect to our previous work,⁶ to this effect of N-hydroxyl carbazole on the chromophore.

The dye-functionalized sol-gel hybrid materials were successfully poled at 80–140 °C, without degradation of the film surface and the second-harmonic (SH) signal was measured. During the poling process the alignment continuously increases in the first 4 h and then stabilizes. After the poling field was switched off the SHG signal immediately dropped at a lower value as it is observed in similar sol-gel materials. The SH signal of the samples under investigations was compared with the SH intensity generated by a Y-cut quartz crystal via the standard Maker fringes technique.^{11,12} This provided an estimate for the non-linear coefficient d_{33} of the samples at a value of $\sim 50 \div 70$ pm V⁻¹ at the wavelength of 1.064 μ m.

Value of 0.34 for the order parameter Φ was estimated by assuming the d_{33} measurement.^{13,14} This value is quite large compared with those reported in literature for poled NLO chromophores in sol-gel systems.

After two months d_{33} stabilized around 70% of the initial value and remained almost constant over the measurements performed during several months. This

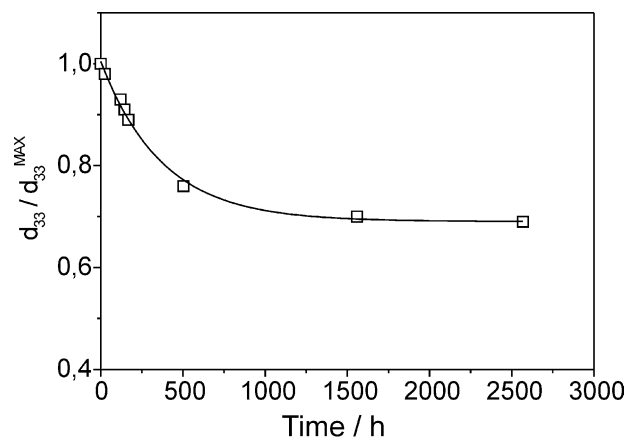


Fig. 4. Decay of the second harmonic coefficient d_{33} for BisOH.-PETCN doped hybrid films after poling. Solid line is the best exponential decay fit.

decay (shown in Fig. 4) can be attributed both to a partial disorientation of active chromophores and to a slight residual photobleaching. Solid line in Fig. 4 represents a fit based on an exponential function added to a constant term, which is likely to show the presence of a second, very long decay time.

4. Conclusions

The possibility of using zwitterionic push-pull chromophores in hybrid matrices to prepare materials with second order non-linear optical properties has been demonstrated. The introduction of amine functional groups in the matrix has shown to reduce photobleaching effects in the chromophores and the d_{33} coefficient reaches values comparable with the largest reported in literature, notwithstanding the relatively low chromophore concentration.

References

1. Kuzyk, M. G. and Dirk, C. W., *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*. Marcel Dekker, New York, 1998.
2. Abbotto, A., Pagani, G., Brusatin, G., Innocenzi, P., Guglielmi, M., Meneghetti, M., Signorini, R. and Bozio, R., Novel hybrid organic-inorganic sol-gel materials based on highly efficient heterocyclic push-pull chromophores. *SPIE*, 1999, **3803**, 18.
3. He, G. S., Yuan, L. X., Prasad, P. N., Abbotto, A. and Pagani, G. A., *Optic. Commun.*, 1997, **140**, 49.
4. Abbotto, A., Facchetti, A., Pagani, G. A., Yuan, L. X. and Prasad, P. N., *Gazz. Chim. Ital.*, 1997, **127**, 165.
5. Abbotto, A., Bradamante, S., Facchetti, A., Pagani, G. A., Ledoux, I. and Zyss, J., *Mat. Res. Symp. Proc.*, 1998, **488**, 819.
6. Innocenzi, P., Miorin, E., Brusatin, G., Abbotto, A., Beverina, L., Pagani, G. A., Casalboni, M., Sarcinelli, F. and Pizzoferrato, R., Incorporation of zwitterionic push-pull chromophores in hybrid organic/inorganic matrices. *Chem. Mater.*, 2002 in press.

7. Abbotto, A., Bradamante, S., Facchetti, A. and Pagani, G. A., *J. Org. Chem.*, 1997, **62**, 5755.
8. Mortazavi, M. A., Knoesen, A., Kowel, S. T., Higgins, B. G. and Dienes, A., *J. Opt. Soc. Am. B*, 1989, **6**, 733.
9. Casalboni, M., Sarcinelli, F., Pizzoferrato, R., D'Amato, R., Furlani, A. and Russo, M. V., *Chem. Phys. Lett.*, 2000, **319**, 107.
10. Lissi, E. A., Encinas, M. V., Lemp, E. and Rubio, M. A., *Chem. Rev.*, 1993, **93**, 699.
11. Jerphagnon, J. and Kurtz, S. K., *J. Appl. Phys.*, 1970, **41**, 1667.
12. Singer, K. D., Sohn, J. E. and Lalama, S. J., *Appl. Phys. Lett.*, 1986, **49**, 248.
13. Graf, H. M., Zobel, O., East, A. J. and Haarer, D., *J. Appl. Phys.*, 1994, **75**, 3335.
14. Cao, X. and McHale, J. L., *J. Phys. Chem. B*, 1997, **101**, 8843.